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A NEW MINIMAL GAUSSIAN BASIS SET FOR MOLECULAR CALCULATIONS

by

© ATHANASIOS N. TAVOUKTSOGLOU

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the faculty of Graduate Studies and Research, for acceptance, a thesis entitled A NEW MINIMAL GAUSSIAN BASIS SET FOR MOLECULAR CALCULATIONS submitted by ATHANASIOS N. TAVOUKTSOGLOU in partial fulfilment of the requirements for the degree of Master of Science.

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Date April 21, 1979.

TO MY PARENTS.

Τότε γάρ οἰόμεθα γιγνώσκειν ἕκαστον,
ὅταν τά αἴτια γνωρίσωμεν τά πρῶτα
καί τάς ἀρχάς τάς πρώτας
καί μέχρι τῶν στοιχείων.

Ἀριστοτέλης:"Φυσικά" 1.1.184α-3-5

Because we then judge that we have knowledge of something,
when we come to know the first causes
and the first principles
down to the most fundamental elements.

Aristotle: "Physics" 1.1.184a 3-5

ABSTRACT

The problem of obtaining a minimal Gaussian basis set is treated in the present thesis. There are a number of such sets already available, but they all have serious limitations and shortcomings. The most celebrated of these existing minimal Gaussian basis sets are reviewed, and their defects are found and proved. A review of the method of obtaining basis set expansions is also made.

A new basis set is proposed here. Atomic orbitals are expanded in terms of three Gaussian functions. The expansions are determined by a least squares fitting process developed by S. Huzinaga et al. The orbital exponents and expansion coefficients are then energetically optimized.

Applications of the new basis set are made on a number of atoms. The results are very encouraging considering the level of sophistication of the method. It is demonstrated that STO-SZ and STO-3G are very ineffective when applied to third row atoms. In contrast, the values produced by this work for the mentioned atoms are very good. The method, therefore, proves highly appropriate for treating transition metal elements.

Quantum mechanical calculations of some closed-shell molecular systems were also performed. The molecular and molecular orbital energy values thus determined were

found to be significantly better than those obtained using STO-3G. Molecular geometries are also calculated to a satisfactory degree of accuracy.

The method leads to contracted Gaussian basis sets, which are compact, easy to use, and very economical in terms of computing time. It can thus safely be recommended for calculations of polyatomic molecules. It should particularly be used in cases involving third row or heavier atoms, where the STO-KG method breaks down.

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I. INTRODUCTION

The first steps in the history of quantum mechanical calculations on the electronic structure of molecules aimed at the determination of a wave function for a single given arrangement of the atoms in space. In most cases this arrangement was the equilibrium geometry, as determined experimentally.

The development of high speed electronic computers has been extremely rapid during the last few decades. The resulting emphasis on quantum mechanical calculations led to the refinement of the theories and methods used in such calculations. Potential energy surfaces with respect to geometrical parameters have consequently been extensively explored, in order to locate the minima of these surfaces, and thus establish the equilibrium values of the structural parameters.

The search for potential energy minima can be done in two ways. One can assume that the values of a number of parameters are constant and vary the rest until a minimum is achieved. Alternatively, the energy can be minimized with a complete and simultaneous variation of all parameters. It is obvious that the latter method would be preferable, whenever such a process is possible.

One is thus led to an a priori prediction of molecular geometries. In the process, the only experimental

data used are those relating to the values of the fundamental physical or chemical constants. This means that the calculated geometry is purely a result of the theory and method. The theoretical structures can then be used in two ways:

(a) to provide a systematic evaluation of the capabilities and potentials of the theory and method. Also, to uncover any possible defects or inherent limitations of the theory, at its certain level of sophistication.

(b) Once the theory and method have been successfully tested, they can be used to calculate the structures of molecules that have not so far been determined by experiment. These calculations can only be good to the established level of accuracy of the theory and method.

Most of the theoretical structural predictions to date have been carried out at the Hartree-Fock level, using a single determinant wave function, with a basis set expansion. A basis set expansion is usually a linear combination of functions that represents the behaviour of an atomic or molecular orbital. The accuracy of the results is closely related to the basis set expansion. For a large basis set, the results will be independent of detail and characteristic of a geometry at the Hartree-Fock limit. For a small basis set, the results strongly depend on the basis set employed.

Since in the majority of cases we are forced to use a limited basis set, the importance of its choice is obviously critical to the calculations; hence it should be made with the utmost care. Physical and chemical intuition and insight are, therefore, very important.

In the next chapter we shall demonstrate the use of two different kinds of basis functions in simple quantum mechanical calculations.

II STO's AND GTO's

II.1 The Hydrogen Molecule with Slater-Type Functions.

Because of its simplicity, the hydrogen molecule has been heavily used as a prototype in demonstrations of various theories and methods. Although some of its properties are quite unique, it can still provide a useful example from which ideas about the use of single-electron wave functions in the expansion of molecular wave functions may be drawn.

Consider the hydrogen molecule at infinite internuclear separation. In this case, the two atoms can be considered independent of each other. Then, the wave function of the ground state of the molecule is[1]:

$$\psi_+(1,2) = \frac{1}{2^{\frac{1}{2}}}N \left\{1s_A(1)1s_B(2)+1s_A(2)1s_B(1)\right\} \left\{\alpha(1)\beta(2)- \right.$$
$$\left. -\beta(1)\alpha(2)\right\} \qquad (1)$$

where

$$1s = \left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} e^{-\zeta r} \qquad (2)$$

and N is the normalization factor.

From equations (1) and (2), it follows that functions of the form:

$$r^{n-1}e^{-\zeta r}Y_{lm}(\theta,\phi) \qquad (3)$$

are suitable for expanding the molecular wave function. These functions (3), are called Slater-type functions[2-5].

It must be remembered, however, that the above discussion only applies at infinite internuclear distance. When the atoms approach each other for molecular formation, the electronic distribution is bound to change. This means that the shape of the orbitals will be altered. For finite internuclear distances, therefore, the wave function (1) is still a good approximation to the true molecular wave function, if it is adjusted to accommodate for the orbital contraction that takes place upon molecular formation.

The experimental dissociation energy for the hydrogen molecule is:

$$D_e^{exp} = 4.72 \text{ eV}$$

The dissociation energy obtained using function (1) is:

$$D_e = 3.14 \text{ eV with } \zeta = 1.0 \text{ in (2)}$$

To account for the change of atomic orbitals, upon molecular formation, minimize the energy with respect to the orbital exponent ζ, in formula (3). This leads to

the following values:

$$\zeta = 1.17, \quad D_e = 3.76 \text{ eV}$$

The same result could be attained by a different method. Instead of using one Slater-type function, use the linear combination of two such functions on each centre, i.e.

$$1s_i = C_1 1s_i(\zeta_1) + C_2 1s_i(\zeta_2) \tag{4}$$

There is an advantage in this latter method, because one substitutes the optimization of the non-linear parameter ζ in (3), by the optimization of two linear parameters (C_1, C_2) in (4), which is an easier task. Choosing $\zeta_1 = 1.0$ and $\zeta_2 = 1.5$, one obtains:

$$C_1 = 0.663, \quad C_2 = 0.351 \qquad D_e = 3.74 \text{ eV}$$

It is possible to further improve the wave function. This is achieved by taking into account the polarization effects, with the inclusion of the $\sigma(2p)$ function to provide a better buildup of charge in the bonding region. The dissociation energy thus attained is[6]:

$D_e = 4.02$ eV

It is also possible to consider a completely general function[7,8], and determine its most appropriate form.

The Heitler-London valence-bond method we just described depended on the assumption that a wave function, valid in the separated atom region, could be extended to apply to the molecular region. But it is equally possible to start at the united-atom region and extend the wave function into the molecular region. This leads to the molecular-orbital method, which is the complete analogue of the atomic-orbital method for atoms. It must be noted, however, that molecular orbitals are normally polycentric, as compared to monocentric atomic orbitals.

Let us consider the molecular orbital for the ground state of the hydrogen molecule. It is reasonable to assume that the wave function near nucleus A will resemble the atomic orbital $1s_A$ of that atom. The same argument applies for the wave function in the vicinity of nucleus B. The Ritz principle thus leads us to write:

$$\Psi_+ = C_1\, 1s_A + C_2\, 1s_B \qquad (1a)$$

where the 1s function is the same as in (2). The coefficients C_1 and C_2 are variable parameters. In this case, due to the symmetry of the hydrogen molecule with

respect to interchange between A and B, we can write:

$$\Psi_+ = 1s_A + 1s_B \qquad (1b)$$

Evaluating the dissociation energy as before, with the value of ζ in (2) equal to unity, we obtain:

$$D_e = 2.70 \text{ eV}$$

However, this value can be considerably improved if we optimize the orbital exponent ζ. In this case:

$$D_e = 3.14 \text{ eV}$$

Further refinements to these values can also be made, as they were made on the Heitler-London wave function.

In the next section the use of a different kind of function will be demonstrated through its application to the hydrogen atom.

II.2 The Hydrogen Atom with Gaussian-Type Functions.

In 1950, S.F. Boys first demonstrated the usefulness of Gaussian-type functions in quantum mechanical calculations. The general form of these functions is:

$$\phi = x^l y^m z^n e^{-\alpha r^2} \qquad (5)$$

Let us employ one such function to describe the ground state of the hydrogen atom. Optimizing the Gaussian-orbital exponent in (5), we obtain:

$$\alpha = 0.283 \quad E = -0.42441 \text{ a.u.}$$

The atomic energy of hydrogen is known to be -0.5 a.u. Thus, use of only one Gaussian function yields approximately 85% of the energy. If, however, we use a linear combination of four such functions, i.e.

$$\psi = \sum_{i=1}^{4} C_i \phi_i \qquad (6)$$

and optimize both the orbital exponents and the expansion coefficients, we have:

$$E = -0.49928 \text{ a.u.}^{10}$$

We thus retrieve 99.86% of the total atomic energy.

For reasons of simplicity, only the hydrogen atom was discussed above using Gaussian functions. A treatment of the molecular case would follow along the lines of the previous section, the only difference being that Gaussian-type functions would now be used.

There is one unavoidable conclusion from the preceding example. It is possible to obtain an accurate enough description of an atom provided that a sufficient number of Gaussian-type functions is used.

In the following section we attempt to make a comparison between the two kinds of functions we have considered thus far. Some of their properties will be mentioned and reasons for the introduction of Gaussian functions to molecular calculations will be given.

II.3 Slater-Type Functions versus Gaussian-Type Functions.

It has already been demonstrated that, at least in principle, Slater-type functions are highly appropriate for use in molecular calculations. They have indeed been extensively used in such calculations with significant success. It is essential to mention that due to their exponential character they provide a very accurate description of the behaviour of the electrons near the nucleus. This is a significant property that Gaussian-type functions do not possess. It is unfortunate, however, that Slater functions lead to extremely difficult many-centre two-electron integrals, the solution of which, when possible, requires unreasonably long computer time. The only exception is the case of diatomic molecules, which have been calculated using Slater-type functions. The results of these calculations have been extremely

successful, and they are the best theoretical calculations for diatomic molecules available.

On the other hand, the work of S.F. Boys[9] has proven that molecular integrals can be evaluated with relative simplicity, if Gaussian functions are used. But we have already seen that Gaussians are inherently poorer than STO's in describing atomic and molecular systems. It is necessary, therefore, to use a larger number of the former for results of comparable accuracy.

In Table 1, the convergence of the Hartree-Fock energy of the oxygen atom as a function of the number of Gaussian functions used in the calculation is shown[11]. An examination of the table verifies two points that have been made above:

(a) that the energy convergence improves drastically with the increasing number of Gaussians used.

(b) that Gaussians are rather poor in describing the electronic behaviour near the nucleus, since it is seen that a larger number of functions are needed to represent the s-orbital for comparable accuracy.

The effect of a larger Gaussian basis set on the computer requirements for molecular calculations is twofold:

(a) The duration of calculation of the electronic wave function is proportional to the number of integrals.

(b) The number of two-electron integrals to be evaluated

Table 1. Convergence of the Hartree-Fock energy of the oxygen atom, with the number of Gaussian functions used[a].

Orbital	No. of functions	Energy error (a.u.)
	3	0.085
p	4	0.020
	5	0.005
	6	0.001
	7	0.025
s	8	0.008
	9	0.005
	10	0.001

(a) Reference 11

increases as the fourth power of the number of basis functions (i.e. as N^4). Since the time required to solve the matrix Hartree-Fock equations depends on the number of two-electron integrals, use of large Gaussian basis sets can make the iterative solution of these equations very time consuming.

A number of techniques were hence devised to accelerate the convergence of solutions. These techniques aimed at reducing the total time required, mainly by reducing the number of iterations.

However, the most direct answer to the time problem should come from an educated reduction of the number of basis functions. This was accomplished by contraction, that is by grouping together some Gaussian functions in the large basis set, and treating them as one. Integrals are thus being stored for this contracted function only. Successful contraction was shown[12,13] not to result in significant loss of energy.

The process of contraction is now standard practice. The reduction of a large Gaussian basis set into a smaller, compact, but flexible enough set of functions is in the heart of modern and efficient molecular calculations. It must be stressed through, that a great deal of caution must be exercised when contracting atomic basis sets.

There is one more difference between Slater and Gaussian-type orbitals that should be mentioned. The

Slater 1s, 2s, 3s, ..., functions behave as $\exp(-\zeta r)$, $r\exp(-\zeta r)$, $r^2\exp(-\zeta r)$,... In contrast, all s-type Gaussians are taken to behave as $\exp(-\alpha r^2)$, i.e. like 1s functions. Similarly all p-type functions behave like the 2p, etc. This was shown[14] not to result in any adverse effects on the accuracy of calculations. Furthermore, it simplifies the integrals considerably.

We have so far discussed various basis functions, but we have not seen how the atomic orbital expansions are made. This will be the topic of the next chapter.

III ON STO EXPANSIONS

III.1 Gaussian Expansions of Atomic Orbitals.

There have been a number of attempts[15-20] to obtain approximate expansions of Slater-type orbitals in terms of Gaussians, but it appears that most of these methods do not produce satisfactory results when applied to molecular quantum mechanics.

K. O-ohata, H. Taketa and S. Huzinaga[21] proposed a least squares method of expansion, with special emphasis on good results. A brief description of their method, which was also used in this work, is given below.

Define the normalized STO as:

$$\psi^{s}_{nlm}(\zeta;r) = R^{s}_{n}(\zeta;r)\ Y_{lm}(\theta,\phi) \qquad (7)$$

where

$$R^{s}_{n}(\zeta;r) = N^{s}_{n}(\zeta) r^{n-1} \exp(-\zeta r) \qquad (8)$$

and

$$N^{s}_{n}(\zeta) = [(2n)!]^{-\frac{1}{2}}\ (2\zeta)^{n+\frac{1}{2}} \qquad (9)$$

Define also the normalized GTO as:

$$\phi^{G}_{nlm}(\alpha;r) = R^{G}_{n}(\alpha;r)\ Y_{lm}(\theta,\phi) \tag{10}$$

where

$$R^{G}_{n}(\alpha;r) = N^{G}_{n}(\alpha) r^{n-1} \exp(-\alpha r^{2}) \tag{11}$$

and

$$N^{G}_{n}(\alpha) = 2^{n+1}[(2n-1)!!]^{-\frac{1}{2}}\ (2\pi)^{-\frac{1}{4}}\ \alpha^{(2n+1)/4} \tag{12}$$

The GTO's are restricted to have even values of $(n-\ell-1)$. In general an N-term expansion of an STO in terms of GTO's is written as:

$$\psi^{s}_{nlm}(\zeta;r) \simeq \sum_{i=1}^{N} C_i \phi^{G}_{i,n'lm}(\alpha_i;r) \tag{13}$$

In equation (13), $\{C_i\}$ are the expansion coefficients.

The term "square deviation of the Gaussian expansion", is taken to mean the deviation of the fitness of the Gaussian expansion with the STO; this is measured by the value of the integral:

$$V(\zeta;C_i,\alpha_i) = \int [\psi^{s}_{nlm}(\zeta;r) - \sum_{i=1}^{N} C_i \phi^{G}_{i,n'lm}(\alpha_i;r)]^2\ dV \tag{14}$$

Integration is considered over the whole space.

Using the scaling theorem, which shall be treated in a later chapter, the problem reduces to obtaining a Gaussian expansion for the STO with an orbital exponent

of unity.

The method of least squares is based on the minimization of the integral in (14), with ζ=1. This is achieved by choosing a set of $\{\phi_i^G\}$. The optimum set of expansion coefficients $\{C_i\}$ is determined by solving the resulting linear equations. Then, the Gaussian orbital exponents are established using the Powell minimization[27]. One of the main difficulties met by this method is the existence of multiple minima. Moreover, it is known that the number of multiple minima increases significantly with the increasing number of variational parameters. However, the results of application of this method are judged[21] good enough for use in molecular calculations.

In the following section, one of the best established least squares representations of Slater-type orbitals as a sum of Gaussian-type orbitals will be discussed.

III.2 The STO-KG Method.

The term "minimal basis set", is used to indicate that only one basis function is used to represent each occupied or partly populated shell of the ground state of an atom. Unpopulated shells are not represented. The contents of the present thesis exclusively concern discussions on such minimal basis sets.

As already mentioned, a number of attempts have already

been made at obtaining GTO expansions of STO's. Outstanding among these attempts is the STO-KG method proposed by J.A. Pople et al.[22-26]. In this method, each atomic orbital is represented by an STO which is least squares expanded in terms of K Gaussians. The principles of the method are outlined in the following equations:

$$\phi'_{\mu}(\zeta,r) = \zeta^{3/2}\phi'_{\mu}(1,\zeta r) \tag{15}$$

$$\phi'_{ns}(1,r) = \sum_{i=1}^{K} d_{ns,i}\, g_{1s}(\alpha_{ni},r) \tag{16}$$

$$\phi'_{np}(1,r) = \sum_{i-1}^{K} d_{ns,i}\, g_{2p}(\alpha_{ni},r) \tag{17}$$

etc.

There are a number of important features in this scheme.

(a) g_{1s}, g_{2p}, etc., are the normalized Gaussian-type functions

$$g_{1s}(\alpha,r) = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2) \tag{18}$$

$$g_{2p}(\alpha,r) = (128\alpha^5/\pi^3)^{1/4}\, r \exp(-\alpha r^2) \cos\theta \tag{19}$$

etc.

(b) The constants d and α are chosen so as to give the

optimum least squares fit to the corresponding STO with $\zeta=1$.

(c) The Gaussian orbital exponents $\{\alpha_{ni}\}$ are common to the ns and np functions. This is done for greater computational economy.

(d) The 2s, 3s, etc., functions are replaced by a linear combination of 1s functions.

(e) All expansions correspond to an STO with exponent $\zeta=1.0$. These exponents are later optimized, and the scaling theorem is applied to the expansions.

The above method has been extensively applied to a number of atomic and molecular systems. It enjoys a fair amount of success in predicting the geometrical structures of many neutral molecules in their ground states.

Increasing the value of K, i.e. increasing the size of the expansion, makes the results of the STO-KG method approach those of the Slater-type basis itself. It is obvious, however, that the method can not surpass the accuracy of STO-SZ (STO single-zeta) calculations. Thus, it is unfortunate that STO-KG is expected to be inappropriate for use in treating third row atoms due to this inherent limitation. This point will be raised again and discussed to a greater depth in a later chapter.

The next chapter introduces a new type of minimal Gaussian basis set, which aims at overcoming some of the limitations of the STO-KG method.

IV A NEW MINIMAL GAUSSIAN BASIS SET

The minimal Gaussian basis set proposed in this work aims at better orbital energies, with particular emphasis on the bonding valence-orbitals of atoms for more accurate quantum mechanical molecular calculations. The orbital expansions still remain at the three-term (3G) level, but a new approach to their formation is suggested.

IV.1 The Atomic Orbital Expansions.

Each atomic orbital will be expressed as a linear combination of three Gaussian-type functions. The expansion method is the following:

For the 1s orbital, a three-term expansion is written as:

$$\phi_{1s} = \sum_{k=1}^{3} C_{1s,k}\, g_{1s,k}(\alpha_{1s,k};r) \qquad (20)$$

This expansion is fitted against the reference[28] STO double-zeta 1s function, according to the least squares fitting scheme proposed by S. Huzinaga et al.[21] and discussed in section III.1. The optimum values of the constants $\alpha_{1s,k}$ and $C_{1s,k}$ are thus determined.

In a completely analogous manner, we expand the 2s orbital as:

$$\phi_{2s} = \sum_{k=1}^{3} C_{2s,k}\, g_{2s,k}(\alpha_{2s,k};r) \qquad (21)$$

To the expansion (21) we now incorporate the ϕ_{1s} contracted function from (20). This augmentation of (21) has a very important purpose. Inclusion of the ϕ_{1s} serves to describe the inner part of the 2s orbital, so that the $\alpha_{2s,k}$ and $C_{2s,k}$ are freer to describe better the outer part of the orbital. The 2s expansion now becomes:

$$\phi'_{2s} = C_{\phi 1s} + \sum_{k=1}^{3} C_{2s,k}\, g_{2s,k}(\alpha_{2s,k};r) \qquad (22)$$

It is this expansion (22) that we now fit against the corresponding[28] STO double-zeta function for the atom. Thus, the optimum values of the constants $\alpha_{2s,k}$ and $C_{2s,k}$ are determined.

We now refit the 1s expansion to the STO double-zeta[28] 1s function for the atom. This time, however, we include in the expansion the contracted ϕ_{2s} from (21). As before, the contracted 2s will describe the outer part of the 1s orbital, so that the $\alpha_{1s,k}$ and $C_{1s,k}$ are freer to describe better the inner part. The new 1s orbital expansion now is:

$$\phi'_{1s} = \sum_{k=1}^{3} C_{1s,k}\, g_{1s,k}(\alpha_{1s,k};r) \qquad (23)$$

From the fitting we obtain a new set of $(\alpha_{1s,k}, C_{1s,k})$, k=1-3.

The expansions (22) and (23) are now fitted successively against the STO double-zeta corresponding

functions[28], until the resulting least squares standard deviations are minimized.

The 2p orbital is similarly expanded and fitted.

$$\phi_{2p} = \sum_{k=1}^{3} C_{2p,k}\, g_{2p,k}(\alpha_{2p,k};r) \qquad (24)$$

If 3p or higher orbitals are present, their method of treatment is completely analogous to that described for the 1s and 2s functions.

At the end of the fitting process, there exists a set of three $(\alpha_{n,k}, C_{n,k})$ pairs, that completely characterize the three-term expansion for each atomic orbital. I.e.

$$\begin{aligned} &1s: \quad [(\alpha_{1s,1};C_{1s,1}),\ (\alpha_{1s,2};C_{1s,2}),\ (\alpha_{1s,3};C_{1s,3})] \\ &2s: \quad [(\alpha_{2s,1};C_{2s,1}),\ (\alpha_{2s,2};C_{2s,2}),\ (\alpha_{2s,3};C_{2s,3})] \\ &2p: \quad [(\alpha_{2p,1};C_{2p,1}),\ (\alpha_{2p,2};C_{2p,2}),\ (\alpha_{2p,3};C_{2p,3})] \\ &\text{etc.} \end{aligned} \qquad (25)$$

Each of the above sets provides a contracted basis function which will be further energetically optimized by the method described in the next section.

IV.2 Energetic Optimization of the Orbital Expansions.

The atomic programme used for all atomic calculations is a standard Hartree-Fock-Roothaan SCF programme, written in Fortran by S. Huzinaga, and based on the Roothaan expansion method.

To optimize the basis set as determined in the previous section and reported in the sets (25), a standard method was employed for consistency. We shall describe this method for atoms having 1s, 2s, and 2p (fully or partially occupied) shells. The procedure consists of the following steps:

Stel 1: Perform an atomic calculation, with all basis functions contracted. The basis set in this case is: GTO(33/3).

Step 2: Release the contracted function for the 1s orbital, keeping all the others contracted. Thus, optimize the 1s orbital expansion coefficients and orbital exponents. The basis set in this case is: GTO(1113/3).

Step 3: Using the orbital exponents and contraction coefficients obtained in step 2, contract the 1s orbital and release the 2s to optimize the $\alpha_{2s,k}$ and $C_{2s,k}$, k=1-3. In this case, the basis set is: GTO(3111/3).

Step 4: Recontract the 2s orbital with the contraction

coefficients and orbital exponents determined in step 3. Release to optimize the parameters of the 2p orbital. The basis set is: (33/111).

Step 5: Using the values of $\alpha_{2p,k}$ and $C_{2p,k}$ obtained in step 4, recontract the 2p orbital. With all basis functions contracted, perform an atomic calculation. This step is the same as step 1, and the basis set is GTO(33/3).

If 3s and 3p orbitals also exist, insert analogous steps after steps 3 and 4 respectively. If in addition, the 3rd orbital is also partly or wholly occupied, a similar step is inserted before step 5. The same reasoning applies for even higher orbitals.

At the next stage of the process, steps 2 through to 5 are successively repeated in cycles. At the end of each cycle the value of the atomic energy drops, as compared to the previous cycle. The repetition of these cycles stops, when the drop in energy from one cycle to the next becomes insignificantly small. It was found that three to four such cycles were sufficient for calculations with the first row atoms. For atoms of the second and third periods, two to three cycles were judged enough to provide the desired results.

The values for the orbital exponents and contraction coefficients determined by the above method are given in Table 2 for the first row atoms in their ground states.

Table 2: Orbital Exponents and Coefficients for the first row atoms.

Orb	LITHIUM ^2S		BERYLLIUM ^1S		BORON ^2P		CARBON ^3P	
	Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient
1s	3.18636(1)	8.13763(-2)	6.51107(1)	7.23370(-2)	1.04649(2)	7.13628(-2)	1.53396(2)	7.07666(-2)
	4.85960	4.11415(-1)	9.73573	3.96311(-1)	1.57015(1)	3.95489(-1)	2.30596(1)	3.95356(-1)
	1.01709	6.45029(-1)	2.03521	6.63844(-1)	3.33012	6.63583(-1)	4.92985	6.63169(-1)
2s	6.85395(-1)	9.43474(-2)	1.42353	-1.07495(-1)	2.71605	-9.73596(-2)	4.39495	-9.26218(-2)
	7.86253(-2)	-3.95702(-1)	3.31501(-1)	2.00869(-1)	4.63654(-1)	2.91851(-1)	6.58157(-1)	3.40674(-1)
	3.44531(-2)	-6.63910(-1)	8.37822(-2)	8.84073(-1)	1.35836(-1)	7.92252(-1)	1.98374(-1)	7.43772(-1)
2p					2.54245	1.07028(-1)	4.23235	1.10281(-1)
					5.14380(-1)	4.56207(-1)	8.61673(-1)	4.62034(-1)
					1.23207(-1)	6.31275(-1)	2.01326(-1)	6.27665(-1)

Orb	NITROGEN ^4S		OXYGEN ^3P		FLUORINE ^2P		NEON ^1S	
	Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient
1s	2.10633(2)	7.05931(-2)	2.77555(2)	7.03080(-2)	3.49669(2)	7.03061(-2)	4.24817(2)	7.23199(-2)
	3.17445(1)	3.95908(-1)	4.18923(1)	3.95853(-1)	5.30514(1)	3.94178(-1)	6.48974(1)	4.00961(-1)
	6.82708	6.62113(-1)	9.04437	6.61894(-1)	1.15218(1)	6.54052(-1)	1.42138(1)	6.54595(-1)
2s	6.59787	-8.90379(-2)	9.28383	-8.75258(-2)	1.25935(1)	-8.82699(-2)	1.65611(1)	-8.49366(-2)
	8.79820(-1)	3.79306(-1)	1.14812	4.07671(-1)	1.44274	4.42451(-1)	1.75081	4.57083(-1)
	2.69261(-1)	7.04726(-1)	3.53831(-1)	6.76432(-1)	4.46441(-1)	6.66396(-1)	5.42711(-1)	6.26307(-1)
2p	6.11362	1.15967(-1)	8.09648	1.23326(-1)	1.02971(1)	1.29985(-1)	1.31990(1)	1.30447(-1)
	1.25946(-1)	4.69361(-1)	1.67764	4.75101(-1)	2.14974	4.81018(-1)	2.75564	4.81497(-1)
	2.91612(-1)	6.18892(-1)	3.74101(-1)	6.15173(-1)	4.72432(-1)	6.07978(-1)	5.97477(-1)	6.09297(-1)

Number in parenthesis denotes power of 10.

In Table 3 the values of these parameters are given for Sulphur and Nickel.

IV.3 Atomic Calculations: Results and Discussion.

In the preceding section we arrived at a complete basis set for each atom of the first row of the periodic table, and also for Sulphur and Nickel at their ground states. These basis sets have been given in Tables 2 and 3. The atomic orbital energies determined using the above sets are displayed at Tables 4 and 5. In these tables, the values of STO-SZ, STO-DZ and H.F. calculations are also given for reasons of comparison.

We have also calculated the percent relative error of our atomic orbital energies with the corresponding STO-SZ and H.F. results. These are given by

$$\left(\frac{E_{SZ} - E_{pres}}{E_{SZ}}\right)\% \qquad \text{and} \qquad \left(\frac{E_{HF} - E_{pres}}{E_{HF}}\right)\%$$

respectively. Their values are displayed in Table 6. A minus (-) sign before the number means that our calculated orbital energy is lower than the corresponding STO-SZ, by the percentage indicated by that number.

A number of comments may be made on observation of Table 6.

(a) All calculated 1s orbital energies are poorer than

Table 3: Orbital Exponents and Coefficients for S and Ni.

Orb	Sulphur (^3P)		Nickel (^3F)	
	Exponent	Coefficient	Exponent	Coefficient
1s	1.12075(3)	7.00404(-2)	3.71633(3)	6.46093(-2)
	1.72613(2)	3.90016(-1)	5.67873(2)	3.74593(-1)
	3.84041(1)	6.51111(-1)	1.25777(2)	6.64236(-1)
2s	4.84113(1)	-9.99127(-2)	1.56865(2)	-1.11233(-1)
	5.23960	4.87790(-1)	1.82921(1)	5.37274(-1)
	2.15444	6.06343(-1)	8.12609	5.55694(-1)
3s	2.52106	-1.76859(-1)	1.36957(1)	-2.32084(-1)
	4.03651(-1)	6.77064(-1)	2.25807	5.77746(-1)
	1.47347(-1)	5.01158(-1)	1.02896	6.29956(-1)
4s			1.36146	-1.87838(-1)
			1.24272(-1)	5.62553(-1)
			4.83679(-2)	5.45291(-1)
2p	4.54572(1)	1.28901(-1)	1.98521(2)	1.00796(-1)
	1.04817(1)	4.86214(-1)	4.64787(1)	4.56571(-1)
	2.91319	5.53493(-1)	1.36427(1)	5.77214(-1)
3p	7.53257(-1)	3.04283(-1)	3.43541(1)	-2.43491(-2)
	2.89607(-1)	5.10095(-1)	3.90276	5.15717(-1)
	1.10548(-1)	3.46945(-1)	1.20099	6.38098(-1)
3d			1.32456(1)	1.89371(-1)
			3.34272	5.22981(-1)
			8.10345(-1)	5.66877(-1)

Number in parenthesis denotes power of 10.

Table 4: Orbital Energies (a.u.) for the first row atoms.

Orb	Calculation	Li(^{2}S)	Be(^{1}S)	B(^{2}P)	C(^{3}P)
1s	Present	-2.45121	-4.68463	-7.62482	-11.22575
	STO-SZ[a]	-2.46019	-4.71712	-7.67787	-11.30156
	STO-DZ[a]	-2.47768	-4.73283	-7.69443	-11.32343
	H.F.[a]	-2.47773	-4.73267	-7.69533	-11.32554
2s	Present	-0.19546	-0.30538	-0.48909	-0.69631
	STO-SZ[a]	-0.19489	-0.30864	-0.48391	-0.67750
	STO-DZ[a]	-0.19632	-0.30923	-0.49408	-0.70436
	H.F.[a]	-0.19632	-0.30927	-0.49469	-0.70563
2p	Present			-0.30245	-0.42081
	STO-SZ[a]			-0.30038	-0.40162
	STO-DZ[a]			-0.30989	-0.43263
	H.F.[a]			-0.30986	-0.43335

Orb	Caculation	N(^{4}S)	O(^{3}P)	F(^{2}P)	Ne(^{1}S)
1s	Present	-15.49477	-20.49257	-26.16144	-32.49478
	STO-SZ[a]	-15.59378	-20.61394	-26.30293	-32.66213
	STO-DZ[a]	-15.62541	-20.66258	-26.37363	-32.75983
	H.F.[a]	-15.62909	-20.66866	-26.38273	-32.77248
2s	Present	-0.93164	-1.22311	-1.54389	-1.89039
	STO-SZ[a]	-0.89254	-1.15089	-1.43065	-1.73250
	STO-DZ[a]	-0.94316	-1.24045	-1.56651	-1.92187
	H.F.[a]	-0.94531	-1.24433	-1.57254	-1.93043
2p	Present	-0.54795	-0.60013	-0.68475	-0.78808
	STO-SZ[a]	-0.50336	-0.50327	-0.52641	-0.56172
	STO-DZ[a]	-0.56587	-0.62827	-0.72391	-0.84143
	H.F.[a]	-0.56758	-0.63192	-0.73001	-0.85044

(a) Ref. 28

Table 5: Orbital Energies (a.u.) for Sulphur and Nickel

Orb	Calc.	$S(^3P)$	$Ni(^3F)$
1s	Present	-91.40960	-303.62705
	STO-SZ[a]	-91.88467	-305.50819
	STO-DZ[a]	-92.00112	-305.58756
	H.F.[a]	-92.00447	-305.61882
2s	Present	-8.98057	-37.72615
	STO-SZ[a]	-8.77098	-37.21212
	STO-DZ[a]	-9.00305	-37.89093
	H.F.[a]	-9.00431	-37.91793
3s	Present	-0.87656	-4.79509
	STO-SZ[a]	-0.81168	-4.34110
	STO-DZ[a]	-0.87897	-4.84609
	H.F.[a]	-0.87955	-4.88783
4s	Present		-0.25482
	STO-SZ[a]		-0.22276
	STO-DZ[a]		-0.26640
	H.F.[a]		-0.27624
2p	Present	-6.62400	-32.71390
	STO-SZ[a]	-6.43647	-32.63106
	STO-DZ[a]	-6.68121	-32.89703
	H.F.[a]	-6.68253	-32.94182
3p	Present	-0.43356	-3.17493
	STO-SZ[a]	-0.38720	-2.85015
	STO-DZ[a]	-0.43694	-3.23877
	H.F.[a]	-0.43737	-3.27764
3d	Present		-0.54799
	STO-SZ[a]		-0.00054
	STO-DZ[a]		-0.66185
	H.F.[a]		-0.70693

(a) Ref. 28

Table 6. Percent Error of Atomic Orbital Energies as compared to STO-SZ[a] and H.F.[a] values.

		Li	Be	B	C	N	O	F	Ne	S	Ni
1s	STO-SZ	0.37	0.69	0.69	0.67	0.63	0.59	0.54	0.51	0.52	0.62
	H.F.	1.07	1.02	0.92	0.88	0,86	0.85	0.88	0.85	0.65	0.65
2s	STO-SZ	-0.29	1.06	-1.07	-2.78	-4.38	-6.28	-7.92	-9.11	- 2.40	- 1.38
	H.F.	0.44	1.26	1.13	1.32	1.45	1.71	1.82	2.07	0.26	0.51
3s	STO-SZ									- 7.99	-10.5
	H.F.									0.34	1.90
4s	STO-SZ										-14.4
	H.F.										7.75
2p	STO-SZ			-0.69	-4.78	-8.86	-19.2	-30.1	-40.3	- 2.91	- 0.25
	H.F.			2.39	2.89	3.45	5.03	6.20	7.33	0.88	0.69
3p	STO-SZ									-12.0	-11.4
	H.F.									0.87	3.13
3d	STO-SZ										-101380
	H.F.										22.5

(a) Ref. 28

STO-SZ by an average of 0.58%.

(b) All the other orbital energies, (excluding the 2s of Be), are superior to STO-SZ.

(c) For the first row atoms, the accuracy of the 2s energy value increases with atomic number as compared to STO-SZ. Beryllium is again excluded. The percent superiority over STO-SZ varies from -0.29% for Lithium, to -9.11% for Neon.

(d) The same trend is obvious for the 2p orbital energies, where the percentage improvement varies from -0.69% for Boron, to -40.3% for Neon.

(3) For the first row atoms again, it is noted that the accuracy of the orbital energies as compared to STO-SZ increases as one proceeds to higher orbitals. Consider the example of Fluorine. The 1s calculated value is 0.54% poorer than STO-SZ; the 2s is 7.92% better, and the 2p is 30.1% better than STO-SZ. This is an extremely important feature because one is more concerned about the accuracy of the outer bonding orbitals, since these are the ones that mainly participate in molecular bond formation.

(f) Similar trends are observed for Sulphur and Nickel. The most important feature presented here is the value of the Nickel 3d orbital energy. Whereas STO-SZ gives a value of -0.00054 a.u. and STO-3G a value of +0.05211 a.u., our calculated value is -0.54799 a.u.

to be compared with the Hartree-Fock result of -0.70693 a.u. Further comments on this important point will be made later on in this section.

The atomic energies obtained using our basis set are displayed in Table 7. In the same table the atomic energies of STO-3G, STO-4G, STO-SZ, STO-DZ and H.F. are given for comparison. With respect to these values, the following comments can be made.

(a) Our calculated atomic energies are invariably higher than STO-SZ. However, the difference appears to be fairly small.

(b) All our values are lower than STO-3G. The difference keeps growing to the favor of the present method, with growing atomic number.

(c) For Oxygen the atomic energy calculated with the basis proposed in this work approaches the value of STO-4G. For all heavier atoms our method yields results that are superior to those of STO-4G.

(d) For Nickel, the atomic energy calculated here is deeper than that of STO-4G by approximately 5.72 hartrees.

In Table 8 we calculate the relative percent error of our atomic energy results as compared to those of STO-SZ and H.F. The formulae used are:

$$\left(\frac{E_{SZ} - E_{pres}}{E_{SZ}}\right)\% \quad \text{and} \quad \left(\frac{E_{HF} - E_{pres}}{E_{HF}}\right)\% \quad \text{respectively.}$$

Table 7: Atomic Energies (a.u.) of the first row atoms, Sulphur and Nickel

	This Calc.	STO-3G[a]	STO-4G[a]	STO-SZ[b]	STO-DZ[b]	H.F.[b]
Li(^{2}S)	-7.37743	-7.32832	-7.39185	-7.41848	-7.43272	-7.43273
Be(^{1}S)	-14.47300	-14.39180	-14.50884	-14.55674	-14.57237	-14.57302
B(^{2}P)	-24.36919	-24.23160	-24.42216	-24.49837	-24.52792	-24.52906
C(^{3}P)	-37.44843	-37.22866	-37.51069	-37.62239	-37.68675	-37.68861
N(^{4}S)	-54.05785	-53.72010	-54.11585	-54.26890	-54.39759	-54.40092
O(^{3}P)	-74.33404	-73.80425	-74.33740	-74.54037	-74.80432	-74.80937
F(^{2}P)	-98.77149	-97.98709	-98.68185	-98.94211	-99.40561	-99.40930
Ne(^{1}S)	-127.71335			-127.81218	-128.53511	-128.54705
S(^{3}P)	-395.49017	-393.17895[d]	-395.44484[d]	-396.62762	-397.50229	-397.50485
Ni(^{3}F)	-1500.1837	-1491.1271[c]	-1494.4635[c]	-1502.0487	-1506.7517	-1506.8705

(a) Ref. 22

(b) Ref. 28

(c) Our own calculation using the STO-3G basis set.

(d) Ref. 23

Table 8. Relative percent error of calculated atomic energies as compared to STO-SZ and H.F. values.[a]

Atom	STO-SZ	H.F.
Li	0.55	0.74
Be	0.75	0.69
B	0.53	0.65
C	0.46	0.64
N	0.39	0.63
O	0.28	0.63
F	0.17	0.64
Ne	0.08	0.65
S	0.29	0.51
Ni	0.12	0.44

(a) Ref. 28

The average percent error on comparison with the Hartree-Fock values is 0.62%. The pattern of the errors resulting from the comparison with the STO-SZ values indicates that the accuracy of our method improves with increasing atomic number. Again the results for Nickel deserve particular attention.

Table 9 displays a comparison between STO-SZ and Hartree-Fock energies for the 3d orbitals of the third row atoms. It is obvious that STO-SZ is extremely ineffective in treating these atoms. The case of Copper clearly demonstrates the bad and unrealistic results obtained by the use of STO-SZ in these cases. Naturally, one would not expect STO-3G to perform better than the single-zeta method. The unavoidable conclusion, therefore, is that STO-3G should not be used in calculations involving transition metals.

In summary, we can say that our method invariably gives better atomic energies than STO-3G. In addition, our orbital energies are also better, with particular emphasis on the accuracy of the higher out-lying atomic orbitals. We would thus expect to obtain better molecular results. Most important, the poor performance of STO-3G and STO-SZ in treating transition metals has been proven beyond any question. Hence, it can safely be concluded that our method is highly appropriate for calculations involving third row atoms.

Table 9: STO-SZ and H.F. 3d orbital energies (a.u.) for 3rd row atoms.

	STO-SZ[a]	H.F.[a]
Sc(^{2}D)	-0.18988	-0.34357
Ti(^{3}F)	-0.24338	-0.44071
V(^{4}F)	-0.25642	-0.50966
Cr(^{5}D)	-0.25083	-0.56920
Mn(^{6}S)	-0.25159	-0.63884
Fe(^{5}D)	-0.15690	-0.64689
Co(^{4}F)	-0.08085	-0.67548
Ni(^{3}F)	-0.00054	-0.70693
Cu(^{2}S)	0.50637	-0.49074

(a) Ref. 28

V MOLECULAR CALCULATIONS

V.1 The Molecular Programme.

For all our molecular calculations, the MOLECULE[29] package programme has been used. This programme performs calculations within the Hartree-Fock S.C.F. scheme. The integral calculations assume an atom centered GTO basis set.

For our purposes the programme consists of two separate parts:

(a) Integral Calculation (MOLECULE). The integral package was written by J. Almlöf[30], but it includes a number of modifications due to O. Gropen. It also includes the option of using model-potentials to simulate the inner-core according to S. Huzinaga[31]. The programme efficiently uses the molecular symmetry in the evaluation of two-electron integrals. Thus, recalculation of symmetry-redundant integrals is avoided, and the construction of blocks of symmetry matrices and supermatrices is achieved without the time-consuming transformation procedure.

(b) Closed shell S.C.F. This is a standard S.C.F. closed shell programme. It has options for trial vectors, extrapolation procedure, and use of the SHIFT-operator[32] and damped F-matrix procedure for obtaining a better convergence.

In Figures 1 and 2 we give the approximate constructions of the two parts of the programme-package described above.

V.2 The Scaling Theorem.

Reference to this theorem has already been made in chapter III.2. It will also be used again in the next section. This is, therefore, an appropriate point to give an account of the theorem.

The scaling theorem can be stated as follows: Suppose that

$$\psi^{S}(1;r) = \sum_{i=1}^{N} C_i \phi_i^{G}(\alpha_i;r) \qquad (26)$$

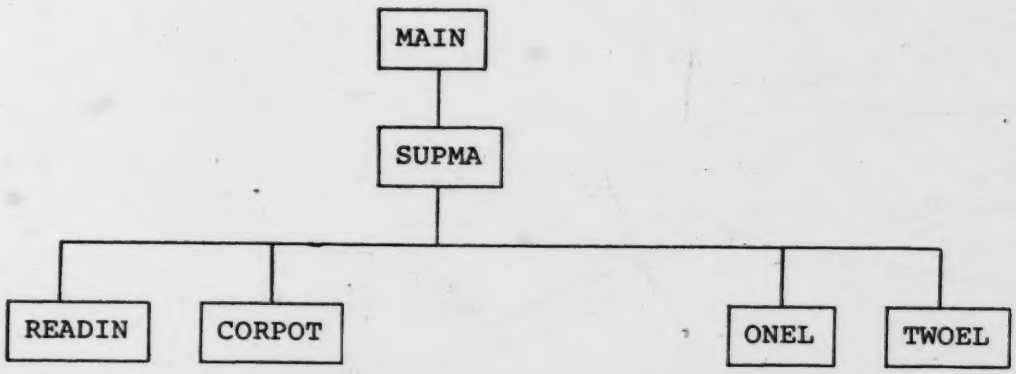
is the Gaussian expansion of a Slater-type orbital, with the exponent value of unity. Then, the Gaussian expansion for the STO with an arbitrary exponent value of ζ, will have the same expansion coefficients $\{C_i\}$, but all the Gaussian exponent parameters $\{\alpha_i\}$ will be multiplied (scaled) by a factor of ζ^2. Thus,

$$\psi^{S}(\zeta;r) = \sum_{i=1}^{N} C_i \phi_i^{G}(\zeta^2\alpha_i;r) \qquad (27)$$

We will first give a dimensional analysis of the theorem. Let us rewrite equation (26) as:

Figure 1

Construction of the Integral Part



READIN: Read input, create necessary symmetry information and normalize contracted basis functions and symmetry functions.

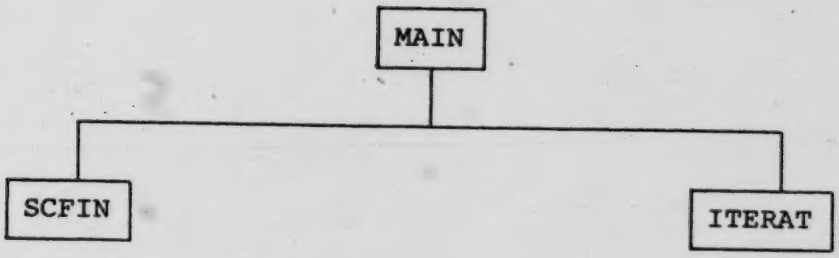
CORPOT: Read input for core-part when model-potential option is used. Organize the core-part information. Use a special subroutine for the calculation of overlap-integrals.

ONEL: Calculate overlap kinetic energy and nuclear attraction energy integrals.

TWOEL: Calculate two-electron integrals.

Figure 2

Construction of the S.C.F. Part



SCFIN: Read input data, organize and print.

ITERAT: Organize the S.C.F. procedure.

$$\psi^S(r) = \sum_{i=1}^{N} C_i \phi_i^G(\alpha_i r^2) \qquad (28)$$

Here, we have made the STO and GTO functions depend on one parameter only instead of two. This is perfectly legitimate since the exponential part of the STO with $\zeta=1$ is $\exp(-r)$; similarly the exponential part of the GTO is $\exp(-\alpha r^2)$.

We now make the mapping $\alpha_i \rightarrow \zeta^2\alpha_i$, where ζ is a real number. Then:

$$\sum_{i=1}^{N} C_i \phi_i^G(\alpha_i r^2) \rightarrow \sum_{i=1}^{N} C_i \phi_i^G(\zeta^2 \alpha_i r^2) =$$

$$\sum_{i=1}^{N} C_i \phi_i^G[\alpha_i (\zeta r)^2] \qquad (29)$$

By observing equation (28), we can say that (29) corresponds to the left-hand side of (28), if the latter is written as:

$$\psi^S(\zeta r)$$

By necessity, ζ should have dimensions of L^{-1}, and ζ^2 should be L^{-2}.

A proof of the theorem is given in Reference 21. We shall consider here a particular feature that makes the transition from (26) to (27) possible. Throughout this

discussion it must be kept in mind that the coefficients $\{C_i\}$ have been shown to be independent of ζ[21].

Consider the right-hand side of relation (26) and take the overlap integral. Since we are dealing with orthonormalized Gaussian functions, one only has to examine the cross-terms $\langle \phi_i^G / \phi_j^G \rangle$. The definitions of ϕ_i^G and ϕ_j^G are taken from equation (10) in chapter III.1. Then:

$$\langle \phi_i^G / \phi_j^G \rangle = [N_n^G(\alpha)]^2 \int_0^\infty r^{2(n-1)} e^{-(\alpha_i+\alpha_j)r^2} \, r^2 \, dr =$$

$$= \frac{2^{2(n+1)} \, \alpha^{(2n+1)/2}}{[(2n-1)!!](2\pi)^{\frac{1}{2}}} \frac{[(2n-1)!!]}{2^{(n+1)}(\alpha_i+\alpha_j)^n} \left(\frac{\pi}{(\alpha_i+\alpha_j)^{\frac{1}{2}}} \right)^{\frac{1}{2}} (\alpha_i \alpha_j)^{(2n+1)/4}$$

$$= \left[\frac{2(\alpha_i \alpha_j)^{\frac{1}{2}}}{\alpha_i + \alpha_j} \right]^{(n+\frac{1}{2})} \qquad (30)$$

Equation (30) is worth commenting upon. Suppose that instead of α_i and α_j, we had $\zeta^2\alpha_i$ and $\zeta^2\alpha_j$. Then it is obvious that the factor ζ^2 would be eliminated from (30). This fact, combined with the fact that the coefficients $\{C_i\}$ are independent of ζ, make the scaling theorem valid.

V.3 The Method.

The basis sets of Tables 2 and 3 were used in a

number of calculations on molecular systems. It was found that although these calculations yielded reasonable values of molecular and molecular orbital energies, they did not produce any binding energies. This defect was attributed to the fact that the basis sets developed by atomic calculations, failed to take into account the effects of molecular formation on the atomic orbitals.

The need, therefore, arose of scaling the Gaussian functions used in these basis sets. For this purpose, the scaling theorem discussed in the preceding section was used.

With the aim of keeping the method at a fairly simple level, it was decided to scale only the outer valence atomic orbitals. Calculational experimentation indicated that this practice did not seem to significantly worsen the results. In accordance, only the 2p orbital was scaled for the first row atoms, and the 3p orbital for Sulphur. The optimum scaling factor of an atom in a particular molecule was determined by successive calculations until the total molecular energy was a minimum. From a series of such optimizations of different molecules, an average scale factor for the valence orbital of that atom was established. The average optimum scaling factors for hydrogen, carbon, nitrogen, oxygen and sulphur are reported in Table 10.

All molecular calculations were performed at the

Table 10: Valence orbital average scaling factors.

Atom	Orb	Scale factor
H	1s	1.450
C	2p	1.065
N	2p	1.065
O	2p	1.065
S	3p	1.100

geometries shown in Table 11. In most cases these structural parameters are Hartree-Fock equilibrium geometries.

In parallel, the package programme GAUSSIAN-70[33] was used to calculate the same molecules, with an STO-3G basis set, at the above values of the geometrical parameters (Table 11). This was done in order to be able to compare the results of the two methods at the same geometry for a certain molecule. It must be noted that when a geometry optimization was performed with GAUSSIAN-70 and STO-3G, the results were the same as those reported by J.A. Pople et al.[22-26].

We also carried out a geometry optimization of the molecular systems we treated. For diatomic molecules this was done by the least squares fitting of the energy curve via a third-degree polynomial. For triatomic or polyatomic molecules, the geometrical parameters were optimized step by step and one by one, making use of the symmetry point group, to which the molecule belongs.

In the next section, we shall present the results of our molecular calculations. A discussion of these results and a comparison with other methods will also be given.

Table 11: Molecular Geometries for Table 12

Molecule	r(a.u.) θ(deg.)
N_2	r = 2.0680
C_2	r = 2.3481
CO	r = 2.1320
CO_2	r = 2.1944 θ = 180.0
H_2O	r = 1.8085 θ = 104.5
SO_2	r = 2.7061 θ = 119.5°
HCN	r_{C-H} = 2.0143 r_{C-N} = 2.1791 θ = 180.0
C_2H_2	r_{C-C} = 2.2810 r_{C-H} = 2.0020 θ_{HCC} = 180.0

V.4 Results and Discussions.

The average values of the atomic valence orbital scaling factors appear in Table 10. Table 11 contains the geometries of the ground states of the molecules used in the calculations. All results given in Table 12 correspond to these geometrical parameters.

The STO-3G results also displayed in Table 12, were calculated here, using GAUSSIAN-70[33]. The values reported are at the geometries of Table 10.

It can be seen that our calculated molecular energies are consistently lower than those of STO-3G. For sulphur dioxide the difference between the two methods is approximately 3.2 hartrees. In molecules involving first row atoms, our method gives energies lower by an average of 0.62 hartrees, than STO-3G. On comparison with the Hartree-Fock or near Hartree-Fock molecular energies, the average relative error of our method comes to 0.75% for the molecules tested. Upon the same comparison, the STO-3G produces results with an average relative error of 1.34%.

In Table 12, the binding energies are also given underneath the molecular energies. In most cases they are of the same order of magnitude as those of STO-3G. Exceptions are the N_2 and CO_2 molecules, where they appear to be fairly small in absolute value. For C_2 and SO_2

Table 12: Molecular and Binding Energies (a.u.)

Molecule	This Method	STO-3G[e]	nr. H.F.
N_2	-108.12076	-107.49484	-108.9928[a]
	-0.00506	-0.05464	-0.1909
C_2	-74.85262	-74.42205	-75.40620[a]
	+0.04424	+0.03527	-0.02898
CO	-111.90495	-111.22458	-112.77901[b]
	-0.12248	-0.19167	-0.28103
CO_2	-186.19402	-185.06472	-187.70366[b]
	-0.07751	-0.22756	-0.39631
H_2O	-75.46393	-74.96291	-76.05936[c]
	-0.13593	-0.16884	-0.25000
SO_2	-543.79626	-540.60254	-547.22464[d]
	+0.36199	+0.18491	-0.12545
HCN	-92.19859	-91.67520	-92.90868[b]
	-0.19533	-0.23153	-0.31914
C_2H_2	-76.28170	-75.85203	-76.84959[b]
	-0.39088	-0.40489	-0.47237

(a) Ref. 34

(b) Ref. 35

(c) Ref. 37

(d) Ref. 36. Also HF(DZ) values: E = -546.99113, E_{BIND} = +0.09364.

(e) Our own calculation using GAUSSIAN-70, with STO-3G basis set.

neither our method nor STO-3G produce any binding energy. It should be stressed, however, that the H.F. (DZ)[36] method also yields no binding for sulphur dioxide.

The results of the geometry optimization are given in Table 13, which displays the calculated equilibrium geometries. With the exception of CO_2, all other structural parameters are closer to the near Hartree-Fock or experimental values than STO-3G.

Finally, in Table 14 we give the molecular orbital energies of N_2 and CO_2 at the internuclear distances of Table 11. The STO-3G values have been obtained using GAUSSIAN-70 at the above geometries. Our results are again closer to the Hartree-Fock energies than STO-3G. The difference between the molecular orbital energy values yielded by the two methods is distinctly pronounced for the outer orbitals. This is also to the advantage of the present method, since most of the molecular properties depend on the location of these outer orbitals.

Table 13: Calculated Molecular Geometries; r(a.u.), θ(deg.).

Molecule	This method	STO-3G	(nr)H.F.	Expt.
N_2	r = 2.1383	2.3300[d]	2.0680[a]	2.0674[d]
C_2	r = 2.4518	2.1429[d]	2.3481[a]	2.3470[d]
CO	r = 2.1112	2.1645[a]	2.1320[b]	2.1320
CO_2	r = 2.2900	2.2450[d]	2.1944[b]	2.1921[d]
	θ = 180.0	180.0	180.0	180.0
H_2O	r = 1.8347	1.8708[d]	1.800[e]	1.8085[d]
	θ = 102.5	100.0	105.0	104.5
SO_2	r = 2.7300	2.8911[f]	2.9329[a]	2.7061[c]
	θ = 112.5	119.45	112.4	119.5
HCN	r_{C-H} = 2.0163	2.0220[d]	2.0143[b]	2.0088[d]
	r_{C-N} = 2.1792	2.1788	2.1791	2.1807
	θ = 180.0	180.0	180.0	180.0
C_2H_2	r_{C-C} = 2.2604	2.2072[d]	2.2810[b]	2.2733[d]
	r_{C-H} = 2.0005	2.0126	2.0020	2.0050
	θ_{HCC} = 180.0	180.0	180.0	180.0

(a) Ref. 34

(b) Ref. 35

(c) Ref. 36

(d) Ref. 24

(e) Ref. 37

(f) Our own calculation using GAUSSIAN-70 and STO-3G basis set.

Table 14: Molecular Orbital energies (a.u.) for N_2 and CO

N_2 (r = 2.0680 a.u.)				CO (r = 2.1320 a.u.)			
Orb	a	STO-3G[b]	H.F.[c]	Orb	a	STO-3G[b]	H.F.[d]
$1\sigma_g$	-15.58252	-15.51928	-15.68195	1σ	-20.44436	-20.42438	-20.67389
$1\sigma_u$	-15.58389	-15.51727	-15.67833	2σ	-11.32088	-11.09336	-11.36987
$2\sigma_g$	-1.48374	-1.44619	-1.47360	3σ	-1.52434	-1.46006	-1.52826
$2\sigma_u$	-0.75550	-0.72202	-0.77796	4σ	-0.76506	-0.69951	-0.81091
$1\pi_u$	-0.62031	-0.57554	-0.61544	5σ	-0.51902	-0.44645	-0.55970
$3\sigma_g$	-0.58456	-0.54039	-0.63495	6σ	0.94367	1.04021	0.42782
$1\pi_g$	0.23248	0.28290		1π	-0.62939	-0.55117	-0.64529
$3\sigma_u$	1.15783	1.13178		2π	0.21260	0.31344	0.16542

(a) Present Method

(b) Our own calculation with GAUSSIAN-70 and STO-3G basis set.

(c) Ref. 34

(d) Ref. 35

VI CONCLUSION

The objective of the present work was to develop a new minimal Gaussian basis set to be used in atomic and molecular calculations. The basis set had to be at a fairly simple level, so that it could be versatile and useful. Since computer time is a major factor to be taken into consideration with most modern quantum mechanical calculations, the basis set had to be economical in terms of time when applied to such calculations. The atomic orbital expansions, therefore, had to be made in terms of a reasonably small number of Gaussian functions. This is a common decision about compromise, that must be taken by people dealing with such topics. In addition, the set ought to overcome some of the problems and inherent limitations of previously developed sets. And of course, any scientific development of a previous theory or model must yield better or at least equivalent results.

A new basis set has indeed been developed by least squares expanding the atomic orbitals of atoms, in three-term Gaussian expansions. The set was optimized to give the least possible standard deviations when compared to accurate atomic orbital representations. It was, in addition, energetically optimized for best possible atomic results. Necessary adjustments have also been made

before it was applied to molecular systems.

As already mentioned, the most widespread parallel method used to date is that of STO-3G. A comparison of our basis set with STO-3G on the atomic level brought to light the following results. Firstly, our basis set invariably produces better atomic energies. The improvement is significant as one proceeds to heavier elements. The difference between our basis set and STO-3G therefore increases as we travel along the periods or down the groups of the Periodic Table. Secondly, the atomic orbital energies produced by the basis set developed here significantly exceed the accuracy of those produced by STO-3G. The difference again becomes particularly worth noting for the outer valence shells of atoms. The importance of having "good" sets of valence atomic orbitals is obvious since these shells are the main participants in molecular formation. Still at the atomic level, we have demonstrated the absolute inefficiency of STO-SZ in treating transition metals. As expected, STO-3G should also be judged inappropriate for use on third-row atoms. The superiority of the present basis sets for treatment of these atoms is unquestionable.

On the molecular level, it has been seen that the results of the present method are once again superior to those of STO-3G, where molecular energies are concerned. The binding energies and calculated equilibrium

geometries are at least comparable and in many cases better than STO-3G. Some exceptions of course do exist. However, the resulting molecular orbital energies are consistently better than STO-3G, being closer to the H.F. values.

We can thus safely conclude that the present method can successfully be applied to a number of molecules, giving very encouraging results. Its outstanding advantage is its efficiency in treating transition metal elements. It can be argued, of course, that STO-3G is more economical in terms of computer time. However, the insignificantly small extra cost of our method seems to be more than offset by the quality of its results and its successful applicability to the third-period elements.

BIBLIOGRAPHY

1. W. Heitler and F. London: Z. Phys. 44, 455 (1927).
2. E. Elementi and D.L. Raimondi: J. Chem. Phys. 38, 2686 (1963).
3. E. Clementi, D.L. Raimondi and W.P. Reinhardt: J. Chem. Phys. 47, 1300 (1967).
4. S. Huzinaga and C. Arnau: J. Chem. Phys. 53, 451 (1970).
5. E. Clementi, R. Matcha and A. Veillard: J. Chem. Phys. 47, 1865 (1967).
6. N. Rosen: Phys. Rev. 38, 2099 (1931).
7. C.A. Coulson and I. Fischer: Phil. Mag. 40, 386 (1949).
8. W.A. Goddard III: Phys. Rev. 157, 81 (1967).
9. S.F. Boys: Proc. Roy. Soc. (London), Ser. A200, 542 (1950).
10. S. Huzinaga: J. Chem. Phys. 42, 1293 (1965).
11. T.H. Dunning, Jr. and P. Jeffrey Hay: Methods of Electronic Structure Theory, Modern Theoretical Chemistry - 3. Edited by H.F. Schaefer III, Plenum Press, N.Y., (1977).
12. T.H. Dunning, Jr.: J. Chem. Phys. 53, 2823 (1970).
13. T.H. Dunning, Jr.: J. Chem. Phys. 55, 716 (1971).
14. S.C. Wang: Phys. Rev. 31, 579 (1928).
15. C.M. Reeves: J. Chem. Phys. 39, 1 (1963).

16. J.V.L. Longstaff and K. Singer: Proc. Roy. Soc. A258, 421 (1960).

17. J.L. Whitten: J. Chem. Phys. 39, 349 (1963).

18. S. Huzinaga: J. Chem. Phys. 42, 1293 (1965).

19. H. Sambe: J. Chem. Phys. 42, 1732 (1965).

20. C.M. Reeves and R. Fretcher: J. Chem. Phys. 42, 4073 (1965).

21. K. O-ohata, H. Taketa and S. Huzinaga: J. Phys. Soc. Jap. 21, 2306 (1966).

22. W.J. Hehre, R.F. Stewart and J.A. Pople: J. Chem. Phys. 51, 2657 (1969).

23. W.J. Hehre, R. Ditchfield, R.F. Stewart and J.A. Pople: J. Chem. Phys. 52, 2769 (1969).

24. M.D. Newton, W.A. Lathan, W.J. Hehre and J.A. Pople: J. Chem. Phys. 52, 4064 (1970).

25. W.J. Hehre, R. Ditchfield and J.A. Pople: J. Chem. Phys. 53, 932 (1970).

26. J.A. Pople: Applications of Electronic Structure Theory, Modern Theoretical Chemistry - 4. Edited by H.F. Schaefer III, Plenum Press, N.Y. (1977).

27. M.J.D. Powell: Computer J. 7, 155 (1964).

28. E. Clementi, and C. Roetti: "Roothaan Hartree-Fock Atomic Wave Functions", Atomic Data and Nuclear Data Tables 14, Academic Press (1974).

29. Carbo-Grapen-Huzinaga, "The Program System, MOMPOS", Edmonton (1977).

30. J. Almlöf: USIP Report 72-09, University of Stockholm (1972).

31. S. Huzinaga and V. Bonifacic: J. Chem. Phys. 60, 2779 (1974); 62, 1507 (1975); 62, 1509 (1975).

32. R. Carbo, J.A. Hernandéz and F. Sanz: Chem. Phys. Lett. 47, 581 (1977).

33. Quantum Chemistry Program Exchange, No. 236, Indiana University.

34. P.E. Cade and A.C. Wahl: Atomic Data and Nuclear Data Tables, 13, 339 (1974).

35. A.D. McLean and M. Yoshimine: "Tables of Linear Molecule Wave Functions", I.B.M. (1967).

36. S. Huzinaga and M. Yoshimine: J. Chem. Phys. 68, 4486 (1978).

37. D. Neuman and J.W. Moskowitz: J. Chem. Phys. 49, 2056 (1968).